Proceedings of the American Academy of Arts and Sciences

VOL. 72. NO. 6.—FEBRUARY, 1938

POLYMORPHIC TRANSITIONS UP TO 50,000 Kg/Cm² OF SEVERAL ORGANIC SUBSTANCES

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INVESTIGATIONS ON LIGHT AND HEAT MADE WITH AID FROM THE RUMFORD FUND

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Presented October 13, 1937 Received November 8, 1937

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Introduction

This paper continues the subject already treated in Proceedings of the American Academy of Arts and Sciences, vol. 72, July 1937. In that paper the transitions of some 35 substances, all of them inorganic, were examined. In this paper the examination is extended to

organic substances. The apparatus and the technique were the same as before, so that no new discussion is needed. In general comment on the new results, it appears that polymorphism is an even more common phenomenon among organic than among inorganic compounds in the temperature range of this work, solid CO_2 temperature to 200°. This might be expected, because it has appeared that the chance that a substance will exhibit polymorphism is roughly greater the lower the melting point, and in general the melting points of organic substances are lower than those of inorganics. To compensate for the greater frequency of polymorphism with organics is the fact that the transitions are generally more sluggish and with smaller volume changes, so that they are much more difficult to measure experimentally; it results that they are of less interest. In fact, a number of cases will appear in the following in which I have not thought it worth while to take the great trouble that would be necessary to determine satisfactorily all the transition parameters, but have let the matter rest with a rather superficial statement of the existence of the transition and its order of magnitude.

The scheme of selecting the compounds for examination in the following was simple. In the absence of any theory, polymorphism may be expected to be incident anywhere. The most significant cases are, in general, those occurring among the substances with simplest structure. After measuring a few common compounds in the Laboratory stock, I adopted the scheme of selecting from the list of organics in International Critical Tables those of the lowest molecular weight, and therefore simplest structurally, which were readily procurable commercially. Unless the contrary is stated, all the compounds used in the following were obtained from the Eastman Kodak Co., and were of their purest grade.

In addition to the measurements with the regular volume apparatus, the shearing phenomena of a number of the substances were investigated as an auxiliary method of exploring for the presence of polymorphism.[1] These shearing phenomena have a certain intrinsic interest of their own, and since it is hardly worth while to write a separate paper describing them, some account will also be given in the following of the results of the shearing measurements. In general characterization, the shearing phenomena of organic substances differ from those of inorganic substances in the much more rapid rise with pressure of the shearing strength of the former. The rise is often linear with pressure, and even often more rapid than linear, so that the curve of shearing strength is concave upward, whereas for

inorganic substances the curve is almost always concave downwards. Initially, organic substances are weak in shear, as is to be expected, but with increasing pressure the strength rapidly increases, and at the maximum pressure of 50,000 the strength averages about that of the usual inorganic compound. There are not, however, any cases of extreme strength corresponding to some of the exceptionally strong inorganic substances, and in general the range of shearing strength in organic substances under high pressure is much narrower than that of inorganics. The rapid increase of shearing strength of organics under pressure reminds one of the very great increase of viscosity of organic liquids under pressure. The mechanism of the two phenomena may well be related, involving an interlocking effect between molecules of complicated shapes.

In the following the shearing measurements on those substances which exhibit polymorphism or which have been explored for polymorphism with negative results are described in connection with the discussion of the phenomena of polymorphism. In addition, the shearing phenomena have been investigated for a number of substances which have not been explored for polymorphism in the volume apparatus; these are described in a separate section.

The presentation of detailed data now follows.

Detailed Data

Carbon Tetrabromide. The phase diagram of this substance has been already investigated.[2] There is a transition at atmospheric pressure at 47°, and there is a third form at higher pressures. In this work an additional form was found at pressures above 10,000, making four modifications in all. Runs were made with two different set-ups of the 50,000 apparatus, at temperatures from room temperature to 175°, eight runs in all.

At temperatures below 130°, the dynamics of this transition are unique, there being an enormous asymmetry. On increasing pressure at temperatures below 130° the transition does not run even up to nearly 50,000, but on releasing pressure the transition runs, irreversibly of course, and with *decreasing* volume. This is highly paradoxical, and at first seems contrary to thermodynamics, that is, a transition with decrease of volume brought about by a decrease of pressure. There is, however, no violation of thermodynamics, the transition being irreversible. The phenomenon is doubtless connected in some way with nucleus formation. Nucleus formation takes time; on the first increase of pressure there was not time for sufficient for-

mation of nuclei, and it was only after release of pressure that sufficient time had been spent in the critical region of nucleus formation to permit the formation of enough nuclei to make possible the transition. In nearly all the experiments the application and release of pressure was done on a careful time schedule, 1,000 kg/cm^2 per minute. The pressure at which the irreversible transition runs with decrease of pressure becomes higher the higher the temperature. This is as would be expected, because at higher temperatures nucleus formation is easier, so that not so long a sojourn in the critical region is necessary, and a higher pressure means a shorter sojourn. At room temperature, the pressure at which the irreversible transition would run on release of pressure has dropped below the reversible transition line, and the transition does not run at all, up to 50,000 and back. At 150° and higher, the speed of nucleus formation has become sufficiently great so that the transition runs irreversibly, with volume decrease as normal, on the first increase of pressure. At 173° the velocity of nucleus formation has increased further, and now the super-pressure required is very much reduced.

Figure 1 shows the phase diagram, and indicates the points at which the transition runs. The points obtained with the two different set-ups are rather consistent. This might not be expected of a thing as capricious as these inhibition phenomena usually are, and indicates that the results have a certain significance.

The reverse transition, from IV to II apparently runs normally enough. It is obvious that the location of the reversible transition line is in great doubt when the limits of indifference are as wide as they are here. I have drawn it with the same general slope as that of the line connecting the points marking the lower pressure of indifference, but this is evidently arbitrary, and in fact it can be argued that the line should be steeper than drawn, since usually the limits of indifference become wider at lower temperatures.

It is hardly worth while giving a table for the transition parameters. The slope of the transition line is in such great doubt that no significance can be attached to any estimated latent heat. The change of volume is small and scattering, the extreme values being 0.004 and 0.009 cm^3/gm. A mean value for ΔV is 0.0075 cm^3/gm. There is no evidence for any significant variation of ΔV with temperature.

A further study of the phenomena of nucleus formation would probably be of interest. I made one set of measurements that shows that the phenomena are not simple. At 100° pressure was increased to 50,000 without the transition running; then on decrease of pressure

the transition ran irreversibly with volume decrease at 23,500, and then on further decrease ran in the opposite direction at 8,300. All this was on the regular time schedule, and was in duplication of the first run, and consistent with it. Pressure was now raised to 23,000,

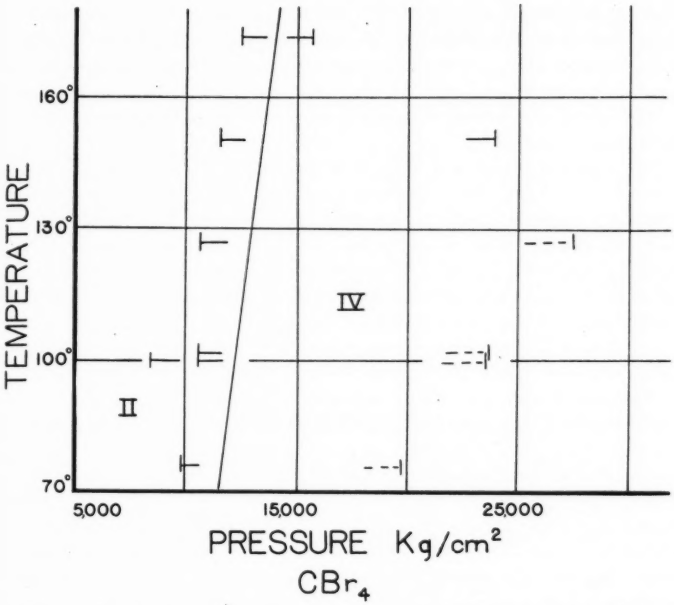

FIGURE 1. The transition pressures of the new high pressure modification of CBr_4 as a function of temperature. The dotted lines indicate that the transition ran with decreasing pressure after an excursion to 50,000. The transitions of II with I and III occur at pressures below 5,000, and have been studied previously.

14,000 beyond the reversible transition point, and left over night, temperature being maintained at 100°. No transition took place over night. This was a great surprise, since I thought that the rate of nucleus formation at 23,000 would be sufficiently great to start the transition in a time approximately 15 times as long as before. In the morning pressure was increased from 23,000 on the regular time schedule, 1,000 kg per minute up to 40,000, with no transition, then

released back to 14,000 (9,000 beyond the place where the transition had taken place on the first release) with no transition, and then back, the transition now starting and running to completion at 24,300 with *increasing* pressure.

CBr_4 is known to decompose appreciably at its melting point at atmospheric pressure at about 90°, and in my former work decomposition was very troublesome. It was apparently complete at 175° and pressures below 7,000. In this work no trace of decomposition was found after the run at 175°. Again we have evidence that pressure is effective in preventing a decomposition that proceeds with increase of volume.

The shearing curve has a marked downward break at room temperature at 15,000 kg/cm² corresponding to the transition above. The high pressure modification thus has a lower shearing strength than the low pressure modification, a somewhat unusual fact. The shearing curve of the high pressure modification rises with general concavity toward the pressure axis. The shearing strength reaches 2,300 kg/cm² at a pressure of 50,000 kg/cm².

Iodoform. Three runs were made with this substance: the seasoning run at room temperature, one at 50°, and one at 150°. There appear to be three small but quite definite transitions. These could be established with greater certainty with increasing than with decreasing pressure, either an asymmetry in the transition or the greater curvature of the isotherm obscuring the effect with decreasing pressure. The lower transition, however, was picked up fairly certainly with decreasing pressure at 150°. The equilibrium lines are shown in Figure 2. Since the transition pressure was not established with decreasing pressure, except for the point mentioned, there is obviously no basis for an estimate of the most probable direction of the transition lines, which are schematically indicated by the dotted lines.

The change of volume at the transition I–II is of the order of 0.0002 cm³/gm; that of the other transitions is perhaps one half as much. There is no point in attempting to calculate the transition parameters.

The shearing curve has a gentle upward inflection in the neighborhood of 30,000, doubtless the transition at highest pressure of those found above brought down to room temperature. The shearing curve of the high pressure modification is concave upward, whereas below the transition the curve is concave downward. The shearing strength at 50,000 is 2,800 kg/cm².

Cyanamide. Two runs were made: the seasoning run at room temperature, and a run at 125°. There appears to be a very small transi-

tion at 125°, at 25,300 kg/cm², and with a volume change of the order of 0.0003 cm³/gm.

Urea. (*Carbamide*). Runs were made with a single filling of the apparatus at room temperature, 80°, 90°, 150°, and 200°. This material has already been found to have two high pressure modifications.[3] The transition line between I and III runs from 4,300 at 0° to 6,750 at 102.3°, the triple point, and the line I–II from the triple point to 7,070 at 160°. With the present set-up, these transitions

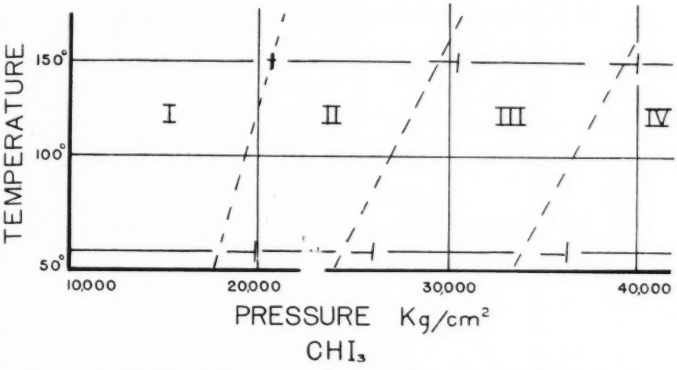

FIGURE 2. The transition pressures of CHI_3 as a function of temperature. The transitions are highly unsymmetrical, occurring with practical speed only with increasing pressure, so that the true location of the transition lines is in much doubt.

were located in practically the positions given, but no attempt was made to repeat the measurements of the parameters. In addition, the existence of at least three new high pressure forms was established with great probability. The volume changes of these are small, however, 0.007 cm³/gm at the most, and since the transitions are sluggish and not easy to measure, I did not try for accurate values of the parameters. At 80° and 90° two transitions were found, the first running between 10,000 and 11,000, and the second at approximately 20,000 at 80° and 19,000 at 90°. At 150° there is probably another transition at approximately 25,000.

At atmospheric pressure urea decomposes with very appreciable velocity at the melting point near 130°. It has been my previous experience that decomposition can often be prevented by the applica-

tion of high pressure. After the exploring run at 150°, temperature was raised to 200° and pressure to approximately 30,000. Pressure was kept here for one hour, and then the apparatus was allowed to cool over night without release of pressure. On opening the apparatus in the morning, no evidence of decomposition could be found. It would seem that there might be interesting possibilities here in the

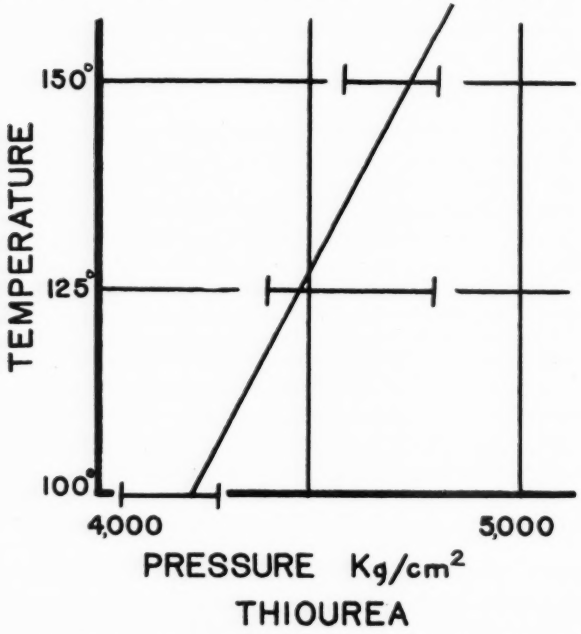

FIGURE 3. The transition pressures of thiourea as a function of temperature.

way of producing new reactions at high pressures between organic compounds at temperatures so high that under normal conditions there would be decomposition.

Very rough values for compressibility could be obtained from the piston displacements. ΔV in cm³/gm was 0.06 between 10,000 and 30,000, and 0.09 between 10,000 and 50,000.

The shearing curve of urea has a very definite abnormality between 22,000 and 28,000. Up to 22,000 the shearing curve is nearly linear.

At 22,000 there is an upward break in direction, but the curve between 22,000 and 28,000 is distinctly concave downward. At 28,000 there is another upward break in direction, less pronounced that that at

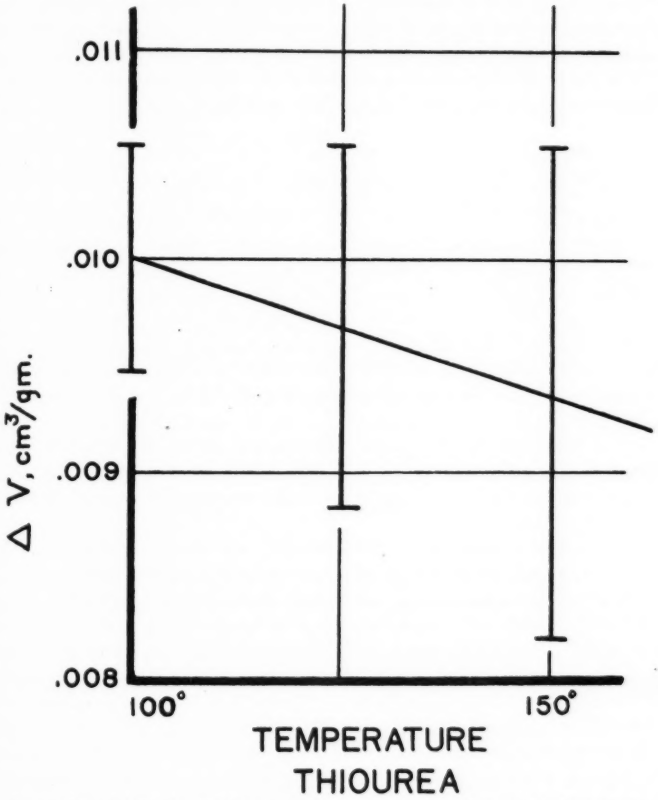

FIGURE 4. The volume changes of thiourea as a function of temperature.

22,000 and beyond 28,000 the curve is nearly linear with a tendency to upward curvature. The abnormality is doubtless due to the two transitions mentioned above, at 20,000 and 25,000, brought down to room temperature and imperfectly resolved. The shearing strength at 50,000 is 2,900 kg/cm^2.

Thiourea. Runs were made with the small and the large apparatus. With the small cylinder exploration was made out to 50,000 at room temperature and 125°. At 125° a transition was found at such low pressures that it was necessary to set up in the larger cylinder in order to get more accurate values. With this apparatus runs were made at 100°, 125°, and 150°.

The phase diagram is shown in Figure 3, the changes of volume in Figure 4, and the transition parameters in Table I.

TABLE I

TRANSITION PARAMETERS OF THIOUREA

Pressure kg/cm²	Temperature	$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
4,230	100°	.0980	$.0100_0$	38.1	.893
4,740	150°	.0980	$.0093_4$	40.3	.945

The shearing curve of thiourea is more concave than usual toward the pressure axis up to 25,000, where there is a flat inflection, with upward concavity beyond this up to 50,000. The shearing strength at 50,000 is 4,000, higher than that of most organic substances. The point of inflection has been the accompaniment of transitions established in the volume apparatus in a number of other cases, but no evidence for it could be found here. One suspects a transition with very small volume change.

Ammonium Thiocyanate. Two set-ups were made. The first, with the regular high pressure apparatus, showed the existence of a transition at very low pressures at room temperatures, and nothing else up to nearly 50,000, and at 125° nothing up to about 45,000. A second set-up was accordingly made with the 3/8 inch apparatus to get more accurate values. Runs were made with this at 0°, room temperature, 51°, and 75°. There is an ice-type transition, with a transition at atmospheric pressure which extrapolates to a temperature of 88°. The volume change is fairly large and runs cleanly, so that fairly good values could be obtained at the two lower temperatures where the pressures are higher. At the two higher temperatures, however, the pressures are so low that accurate values could not be obtained, and in fact the whole range of the phenomenon is at such low pressures as to make it poorly adapted for the present apparatus. The approximate transition parameters are given in Table II. It should be easy to considerably improve on the accuracy of these values if one wanted to construct special apparatus. Instead of giving diagrams as usual,

I have shown the experimental data in the bottom part of Table II. It will be seen on plotting that the experimental points for pressure and temperature lie very smoothly. It is therefore probable that the very distinct upward curvature of the transition line is genuine.

Nitro-guanidine. Runs were made to the maximum pressure at room temperature and 150°. At room temperature evidence of a sluggish transition with small change of volume was found with decreasing pressure at 40,000. This was found both on the seasoning run and on two subsequent repetitions.

TABLE II

TRANSITION PARAMETERS OF AMMONIUM THIOCYANATE

Pressure kg/cm²	Temperature	$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
0	88°	.040	.0419	378	8.9
1,000	53°	.031	.0412	433	10.2
2,000	26°	.024	.0407	507	12.0
3,000	5°	.018	.0402	622	14.7

EXPERIMENTAL DATA

3,310	0°	.0411 .0392
2,130	23°	.0416 .0396
1,080	51°	—
2,130	74°	—

At 150°, the results were complicated. Readings were obtained normally enough starting at low pressures. At 10,000 there was apparently a rapidly running transition, which ran to completion in four minutes, with volume change of 0.0095 cm³/gm. At 22,000 there was another volume discontinuity of 0.0027 cm³/gm, which ran to completion in two minutes. Again at 29,000 there was a smaller volume discontinuity of 0.0018 cm³/gm, running to completion in 2 minutes. There was nothing more up to the maximum. On release of pressure, a small discontinuity was found at 38,000, evidently the same thing that had been found before at room temperature. What was probably the transition at 29,000 was next picked up, but this did not run as sharply as with increasing pressure, but the transition was spread over a pressure interval of 4,000 kg and a time interval of 6 minutes. The next transition which should have been picked up was that at 22,000, but it started at a pressure somewhat above 22,000,

and ran for 90 minutes before being completed, and with a volume change of 0.014 cm^3/gm, against 0.0027 found with increasing pressure.

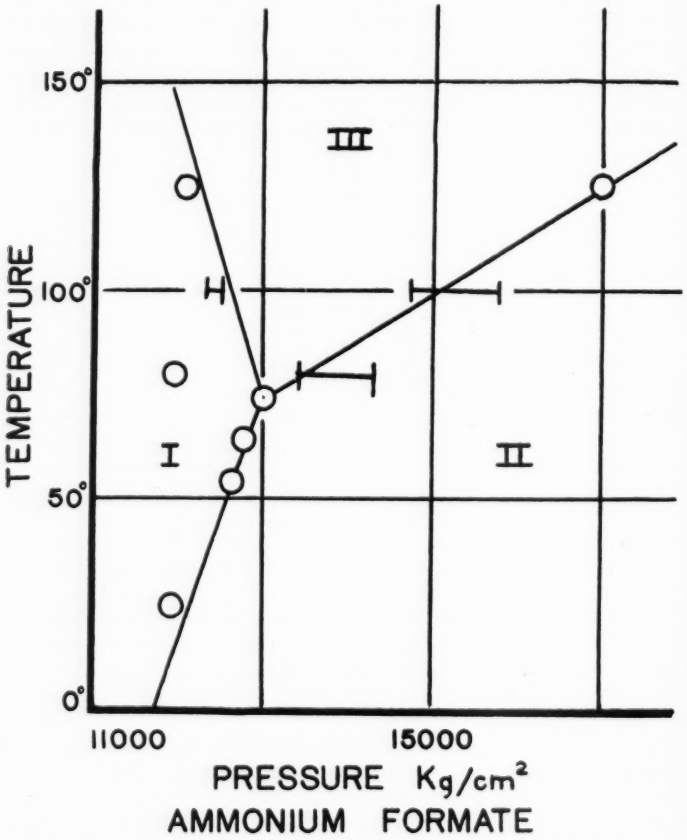

FIGURE 5. The transition pressures of ammonium formate as a function of temperature.

From here on the curve with decreasing pressure was entirely different from that with increasing pressure, the material expanded abnormally rapidly, indicating too great a volume, and already at 6,500 had

reached the initial volume on the first increase. There was no trace of the lowest transition at 10,000. On taking the apparatus apart there was a strong NH_3 smell, and there was blue discoloration of the copper washers. Evidently the material had decomposed in the neighborhood of 25,000. Decomposition must have been complete here, because the subsequent readings showed no creep. The volume change 0.014 represents the difference of volume at 25,000 between the original material and the decomposition products. At atmospheric

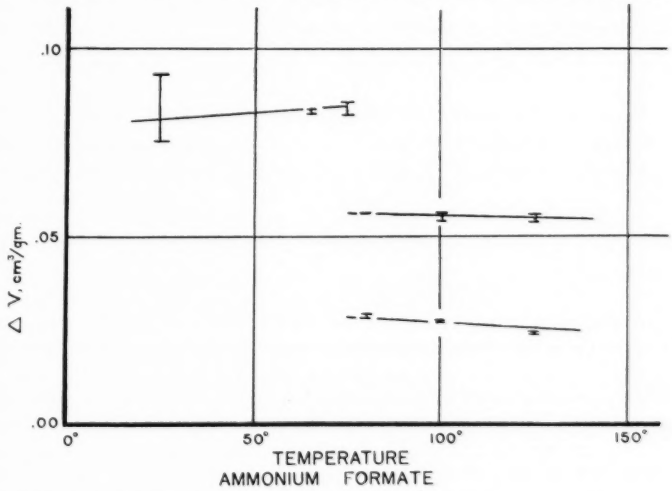

FIGURE 6. The volume changes of ammonium formate as a function of temperature.

pressure the volume difference is much larger, which means that the decomposition products are much more compressible than the initial material.

The puzzle is to understand why the material did not decompose on the initial application of pressure.

Ammonium Formate. Two set-ups were used. The first was with the 0.265 inch apparatus, and with this five runs were made, from room temperature to 150°. The run at 150° was terminated by leak. These runs established the existence of three modifications, and gave fairly accurate values both for the transition pressures and the change of volume. The transitions run cleanly, with large volume change.

No other modifications were found out to the maximum at room temperature or 125°. The second set-up with the more sensitive apparatus was made in order to obtain more data from which the triple point could be located more closely. Runs were made at 80°, 100°, 65°, and 55° with the second set-up.

The phase diagram is shown in Figure 5 and the changes of volume in Figure 6. The transition parameters are sufficiently characterized by their values at the triple point, which are given herewith. The equilibrium lines in Figures 5 and 6 were adjusted so as to satisfy the additive relations at the triple point.

TABLE III

TRANSITION PARAMETERS OF AMMONIUM FORMATE AT THE TRIPLE POINT

Pressure kg/cm²	Temperature		$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		I–II	.0577	.0850	505	21.6
13,000	75°	I–III	−.0674	.0562	−287	−12.2
		III–II	.0125	.0288	792	33.8

Urea Nitrate. Runs were made to the maximum at room temperature (seasoning run and regular run) and at 150°. At room temperature nothing was found. At 150° a very small, but apparently real transition, was found at 24,000. Consistent values for the equilibrium pressure were obtained with both increasing and decreasing pressure, and also consistent values for the change of volume, namely 0.0002 cm³/gm. The transition ran to completion in two minutes.

On further release of pressure, decomposition with large increase of volume began at about 5,000, and continued, automatically increasing the pressure to at least 9,000. Here the temperature was reduced. On opening the apparatus, there was evolution of gas. Decomposition did not occur on the initial application of pressure, because the initial pressure at 150° was chosen as 12,000, with the specific purpose of preventing the anticipated decomposition.

In view of the smallness of the transition it did not seem worth while to set the apparatus up again for further measurement.

Methylamine Hydrochloride. Six runs were made with a single set-up at temperatures from room temperature to 175°.

The phase diagram is complicated, with five modifications. In general, this is one of the easier substances to investigate; the volume changes are fairly large, and the transitions run rather easily, without particularly wide region of indifference or great sluggishness. Only

one transition failed to run sharply enough to make the interpretation of the results secure, namely the transition V–III just above the triple point. However, the location of the transition lines demanded by the other points seemed so unequivocal that I believe there can be no question of the general character of the relations of the phases.

The phase diagram is shown in Figure 7, the changes of volume in

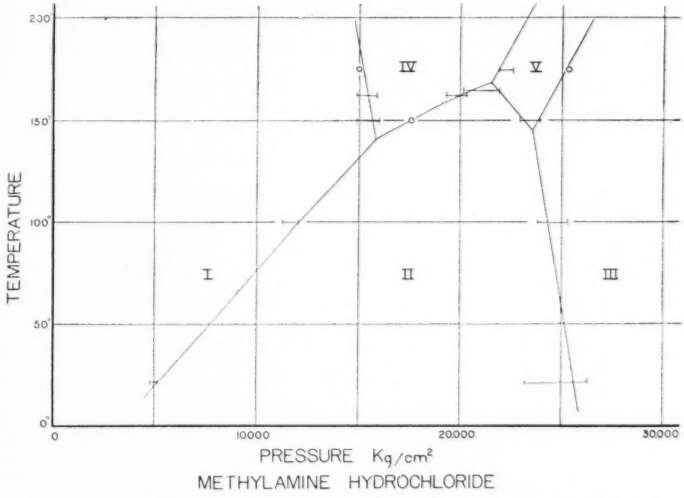

FIGURE 7. The transition pressures of methylamine hydrochloride at different temperatures.

Figure 8, and the transition parameters at the three triple points in Table IV. The location of the transition lines and the magnitudes of the changes of volume have been so adjusted that the additive relations are satisfied at the triple points. It has been possible to do this without doing any serious violence to the experimental points, as the diagrams show. It would probably be possible to make a somewhat better adjustment, for instance drawing the line I–II with normal curvature, in such a way that it would pass between the extreme points at 100°, but any changes which would be made in this way are so slight that it seemed hardly worth while. I do not, as usual, give a table of the transition parameters at various points on the transition lines; it should be possible to get accurate enough values of these

if necessary from the diagrams and the parameters at the triple points.

The rapid variation of volume on the line IV–II is the only particularly unusual feature shown by this substance.

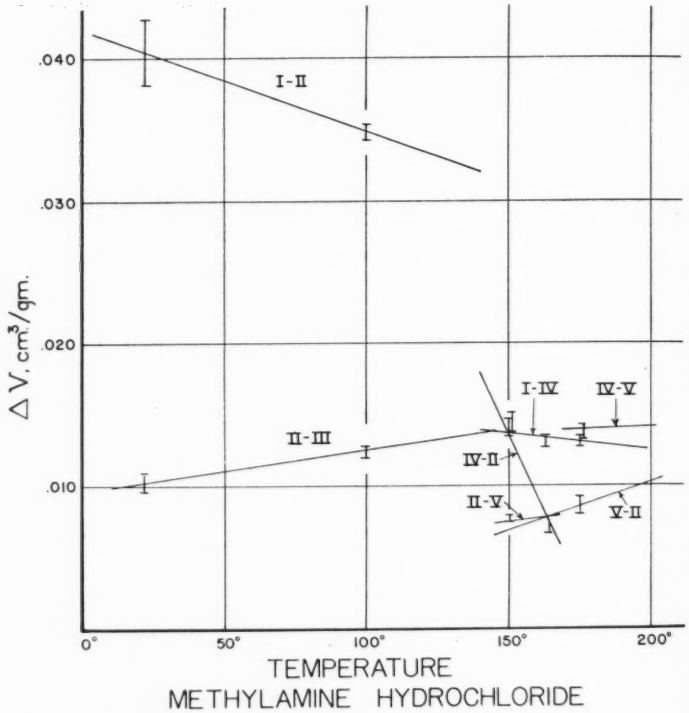

FIGURE 8. The volume changes of methylamine hydrochloride as a function of temperature.

Semi-carbazide Hydrochloride. Two different set-ups were used with this substance; with the first there were five runs at temperatures from room temperature to 150°, and with the second three, from room temperature to 142°.

There is a fairly large transition at low pressures. The transition is

unusual in that the band of indifference is wide, and the width does not fall off noticeably with increasing temperature, while on the other hand, when the transition once starts it runs sharply to completion with no further change of pressure. The runs did not entirely clean up the nature of the behavior at 140° and 150°, but there were anomalies which may or may not be real, the interpretation being obscured by difficulties with the apparatus of one sort and another on the first run, and rupture of the cylinder on the second, together with possible decomposition. On the last run at 142°, a transition was found with

TABLE IV

TRANSITION PARAMETERS OF METHYLAMINE HYDROCHLORIDE AT TRIPLE POINTS

Phases	Pressure kg/cm²	Temperature Centigrade		$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
			I–II	.01100	.0320	−1200	−28.1
I–II–IV	15,800	140°	I–IV	−.058	.0140	100	2.3
			IV–II	.00570	.0180	−1300	−30.4
			IV–V	.0175	.0140	− 354	− 8.3
II–IV–V	21,500	168°	IV–II	.0040	.0060	− 662	−15.5
			II–V	−.0115	.0080	308	7.2
			II–IV	−.0580	.0140	101	2.35
II–III–V	23,500	145°	II–V	−.0115	.0074	269	5.05
			V–III	.0175	.0066	− 158	− 2.70

increasing pressure at 11,000 (higher than would be expected from the results at lower temperatures) and with a volume change only one fifth that to be expected. The run was terminated by rupture, and a certain interpretation does not appear.

At 75°, 100°, and 125° the transition pressures found with increasing and decreasing pressure were respectively: 8,200 and 2,300; 8,800 and 2,100; and 9,800 and 2,100. The corresponding changes of volume were: 0.0198 and 0.0211 cm³/gm; 0.0185 and 0.0218; and 0.0178 and 0.0217. Probably the best mean result is a transition pressure of 5,500 kg/cm² and a change of volume of 0.020 cm³/gm, both independent of temperature.

Dichloro-acetamide. Four runs were made with this: one at room temperature to 50,000, one at 75°, and two at 125°. There is a transition, with fairly large change of volume, in the general neighborhood of 10,000. In spite of the fact that ΔV is large, good values were not

obtained for the transition parameters. At room temperature it appeared as if there were two transitions, an upper one at 13,500 and a

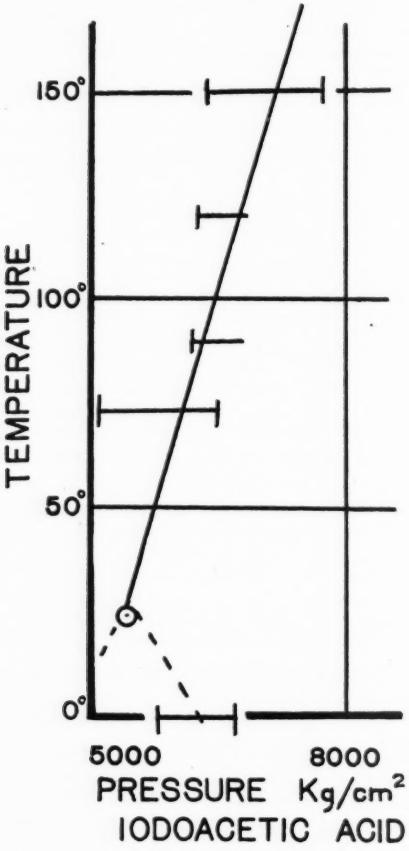

FIGURE 9. The transition pressures and temperatures of iodoacetic acid. It is probable, but not certain, that the transition line forks at the lower end.

lower one at 9,500. At 75°, only a single transition was found, at 7,100. At 125°, the two runs gave for the transition pressure 8,900 and 10,600. The region of indifference was imperceptibly narrow at

all temperatures; the pressures given are means from above and below. The pressures just given do not fit into a sensible phase diagram unless there is abnormally great curvature of the transition lines.

The changes of volume, although fairly large, were difficult to measure because the transition runs at low pressures where the curvature is so great that frictional lag makes an unusually large error.

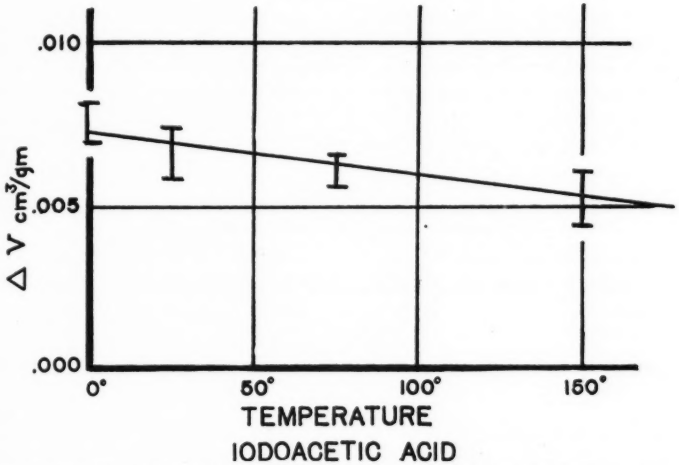

FIGURE 10. The volume changes of iodoacetic acid as a function of temperature.

The values for ΔV varied capriciously between 0.030 and 0.042 cm^3/gm; 0.038 is probably a representative average. In view of the irregularity of the results I do not give a diagram or table of the results.

Iodoacetic Acid. Seven runs were made with a single set-up: the seasoning run and a measuring run at room temperature, and runs at 0°, 75°, 150°, 120°, and 90°. There was leak on the last two runs, so that these runs did not give values for ΔV, and only the equilibrium pressure with decreasing pressure.

There is a transition at low pressures—between 5,000 and 7,000. The equilibrium diagram is shown in Figure 9, the change of volume in Figure 10, and the transition parameters in Table V. It is highly

probable that the transition line forks at the lower end, below room temperature. This is suggested both by the location of the transition point at 0°, lying off the curve with the others, and the fact that at room temperature there was no appreciable width to the band of indifference. This latter is characteristic of the behavior just below a triple point. The possible fork in the transition line is indicated by the dotted lines in Figure 9. It would have been difficult to establish this suspected low temperature transition with certainty because of the sluggishness of the reaction.

Oxamide. With the original set-up the usual seasoning run was made at room temperature, and runs at 100°, 125°, 150°, and 175°. The appearance was that of a most complicated phase diagram, with perhaps a half dozen transitions, none with volume change more than 0.0010 cm³/gm, spread through the range from 15,000 to 45,000.

TABLE V

TRANSITION PARAMETERS OF IODOACETIC ACID

Pressure kg/cm²	Temperature Centigrade	$\frac{dT}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
5,100	0°	.0715	.0072	27.5	0.65
5,800	50°	.0715	.0066	29.9	0.70
6,500	100°	.0715	.0059	30.8	0.72
7,200	150°	.0715	.0053	31.4	0.73

Nine months later two new set-ups were made with runs at 125°, 175° and 200°. Small irregularities were again found, the more prominent of which were definitely repeatable with different set-ups. The most prominent is in the neighborhood of 20,000. It is highly probable that there are a number of transitions so small as to be on the margin of what can be detected with the present apparatus. In view of the complication and difficulty I did not think it worth while to try for more definite results.

At the termination of each of the two repetitions of the experiment it was noticed that the residue had a sweetish odor, distinctly unlike that of the original material. Some chemical transformation is therefore suggested. There was, however, no evidence of gaseous decomposition.

The shearing curve is at first concave downward, then there is a flat inflection near 10,000, upward concavity for a short distance, a second flat inflection near 18,000, then downward concavity with a third flat inflection near 30,000, followed by upward concavity, to a

shearing strength of 4,000 kg/cm² at 50,000. The shearing curve therefore bears out the evidence of the other apparatus for a number of obscure transitions.

Acetamide. This substance is already known to have a transition,[4] the line running from 6,000 at 20° nearly vertically to 5,390 at 127°.0, the triple point with the liquid. Eight runs were made with the 50,000 apparatus between room temperature and 200°, and with the 3/8 inch

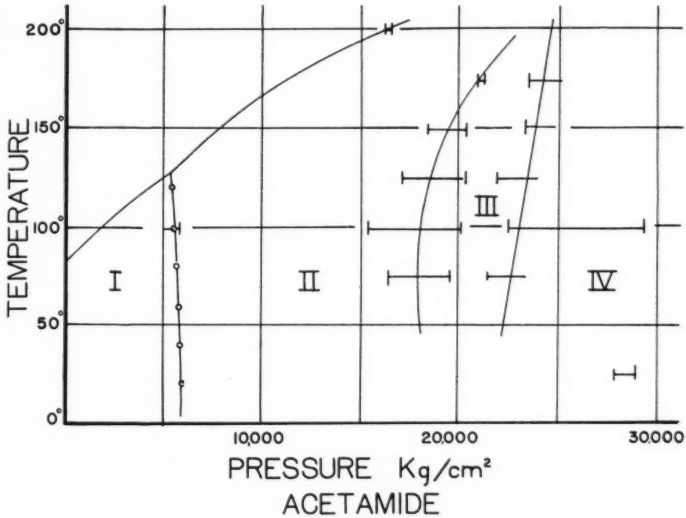

FIGURE 11. The transition pressures and temperatures of acetamide. The circles indicate the previously determined data. Note the isolated transition at 25° near 30,000, between two totally unstable forms.

piston apparatus, a couple of runs at room temperature and 175°. Two new stable forms were found at high pressures, making four stable forms in all. In addition, it is reported in the literature that acetamide readily crystallizes from the melt in an unstable modification. I did not find this unstable form in my previous work, but in the present work, the form initially obtained from the melt and with which the first run was made at room temperature must have been this unstable form. This unstable form experiences a *reversible* transition to what is in all probability still another modification.

This reversible transition of the unstable form was found twice, first on the seasoning application of pressure, and then on the second application, when the coordinates were measured more carefully. It occurs between 27,800 and 28,900 kg/cm², and the values found for ΔV with increasing and decreasing pressure were 0.0031 and 0.0027 cm³/gm. On the second release of pressure the unstable form was

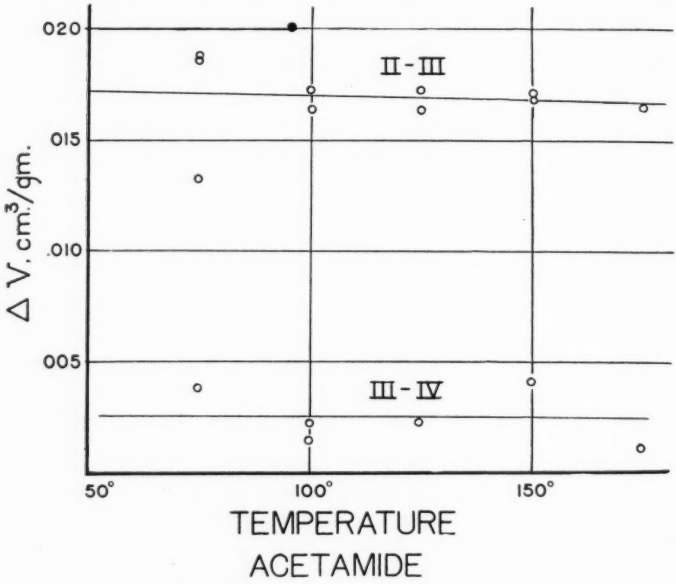

FIGURE 12. The volume changes of acetamide as a function of temperature.

apparently irreversibly replaced by the stable form between 7,500 and 5,000 with a volume *increase* of 0.0215 cm³/gm. The conditions of appearance and disappearance of the unstable form are of course capricious. With the second set-up, with the 3/8 inch piston, the initial material was also the unstable form. At room temperature, pressure was increased to 25,000, released to 0 and increased to 12,000 without the transition running. On raising temperature at 12,000, the unstable form irreversibly transformed into II, with *decrease* of volume. The volume of the unstable form at pressures above 5,000 is thus intermediate between that of I and II. The location of the

various transitions makes it certain that the unstable form at atmospheric pressure is not the high pressure modification II. The unstable form measured at atmospheric pressure by Körber[5] is less dense than I. If my unstable form is the same as that of Körber, its compressibility must be very materially larger than that of I.

The principal interest, of course, is in the reversible transitions of the stable forms. The phase diagram is shown in Figure 11 and the changes of volume in Figure 12, and the parameters of the transitions in Table VI. In addition to the points on the two new lines II–III

TABLE VI

TRANSITION PARAMETERS OF ACETAMIDE

Pressure kg/cm²	Temperature Centigrade	$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		II–III			
18,000	50°	∞	.0172	0	0
18,100	100	.083	.0170	77.	1.8
19,500	150	.0217	.0168	330	7.7
23,000	200	.0100	.0166	790	18.4
		III–IV			
22,200	50	.0625	.0025	13.	.30
23,000	100	.0625	.0025	15.	.35
23,800	150	.0625	.0025	17.	.39
24,600	200	.0625	.0025	19.	.44

and III–IV, a check point was obtained on the line I–II at 100°, giving a transition pressure below 5,800 and a ΔV of 0.0315 cm³/gm, against the equilibrium value 5,590 and ΔV of 0.0321, found formerly. The check is as good as could be expected. In addition, a point was inadvertently obtained on the melting curve at 200°. Good values for the equilibrium pressure were obtained, 16,500 and 16,200 from above and below, but ΔV could not be obtained because of leak, and in fact the experiment had to be discontinued at this point because of leak of the liquid.

The transition III–IV is unusual in that no good values of either the equilibrium pressure or of ΔV could be obtained with increasing pressure. Unusually great super-pressure is needed to start the transition, and even when started it runs very sluggishly. In order to ensure completion of the transition, pressure was usually carried up nearly to the maximum. On decreasing pressure, however, the state of affairs is quite unsymmetrical, the transition running easily, with

sharp ΔV. The exact location of the thermodynamic transition line (that is, the line on which the thermodynamic potentials of the two phases are equal) must be in doubt; in the diagram I have drawn it rather near the lower pressure limit. The line II–III is unusual because of its marked curvature. An alternative explanation would be that the line forks at the lower end, with still another modification, and I cannot claim that this possibility is excluded. However, no trace

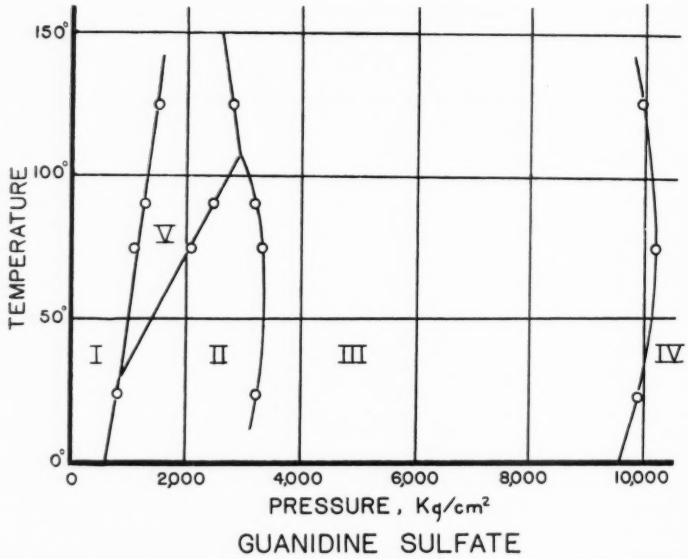

FIGURE 13. The transition pressures and temperatures of guanidine sulfate.

of a new transition line below 80° was found, and the volume relations are not favorable. If there is another transition, it must run with very small change of volume.

Modification IV is distinctly more compressible than III, in spite of its smaller volume. This is the usual relation.

The shearing curve of acetamide has a sharp downward break (high pressure form with lower strength) at about 20,000, where the strength is 2,000 kg/cm². Below and above the break the curve is linear, rising to a strength of 3,600 at 50,000 kg/cm². There can be

little question but that the break is the combination of transitions II–III and III–IV carried down to room temperature and unresolved, because of their closeness.

Guanidine Sulfate. Runs were made with three different set-ups. Two of these were with the regular high pressure apparatus at room

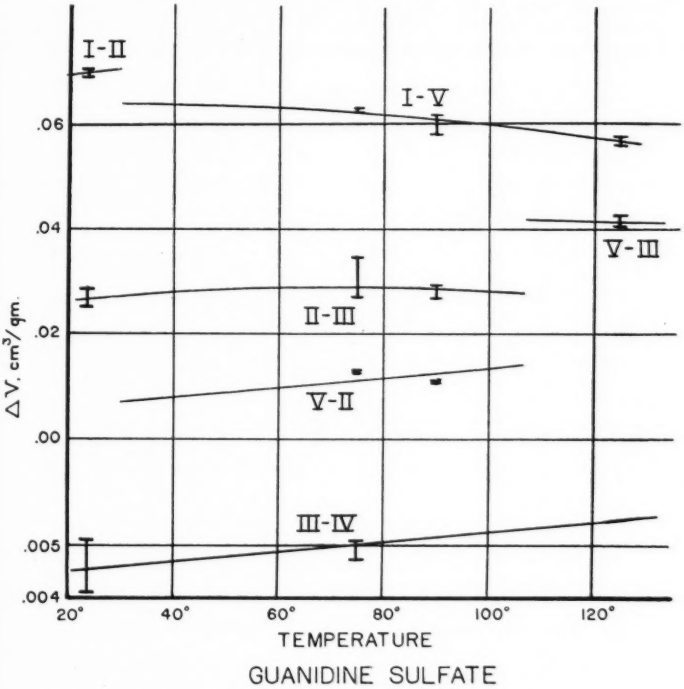

FIGURE 14. The volume changes of guanidine sulfate as a function of temperature.

temperature and 125°; there is a complicated state of affairs at the lower pressures, but nothing else between about 10,000 and the maximum. The third set-up was with the 3/8 inch cylinder, in order to get more accurate values at low pressures, including the transition at 10,000. There are five modifications in all; the transition line at about 10,000 runs without interference with the others, but the other

transitions between 1,000 and 3,000 are so close together that it was a tax on the resolving power of the apparatus to separate them. Measurements were facilitated by the fact that the transitions all run cleanly at all temperatures in the range, with no appreciable region of indifference. There was, however, the usual decrease in the speed of the transitions at low temperatures. The measurement of the low pressure transitions was also facilitated by the fact that the changes of volume are of considerable magnitude.

TABLE VII

TRANSITION PARAMETERS OF GUANIDINE SULFATE

Pressure kg/cm²	Temperature Centigrade		$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
			II–III			
3,170	20°		− .20	.027	−40.	− .93
3,290	40		− .40	.028₅	−22	− .52
3,310	60		+1.00	.029	+10	+ .22
3,250	80		.17	.028₆	60.	1.41
3,060	100		.07	.028	140	3.3
			III–IV			
9,810	20°		−.050	.0045	− 26.	− .6
10,210	50		−.125	.0048	− 12.	− .3
10,300	75		+.84	.0050	+ 2.	+ .05
10,170	100		.119	.0053	17.	.4
9,880	125		.066	.0055	33.	.8
			Triple Points			
850	30°	I–II	.117	.071	184.	4.3
		I–V	.154	.064	126.	3.0
		V–II	.037	.007	57.	1.3
2,950	107°	V–II	.037	.014	143.	3.3
		II–III	−.042	.028	−254.	−5.9
		V–III	−.143	.042	−111.	−2.6

The phase diagram is shown in Figure 13, the changes of volume in Figure 14, and the thermodynamic parameters of the transitions in Table VII. The various values have been adjusted so as to satisfy the thermodynamic conditions of consistency at the triple points. It has been possible to do this without doing much violence to the independent experimental measurements, as the figures show, so that the values cannot be far wrong. However, in some cases it has been

necessary to make a pretty wide extrapolation of the experimental values for ΔV, and there was therefore some latitude in adjusting the

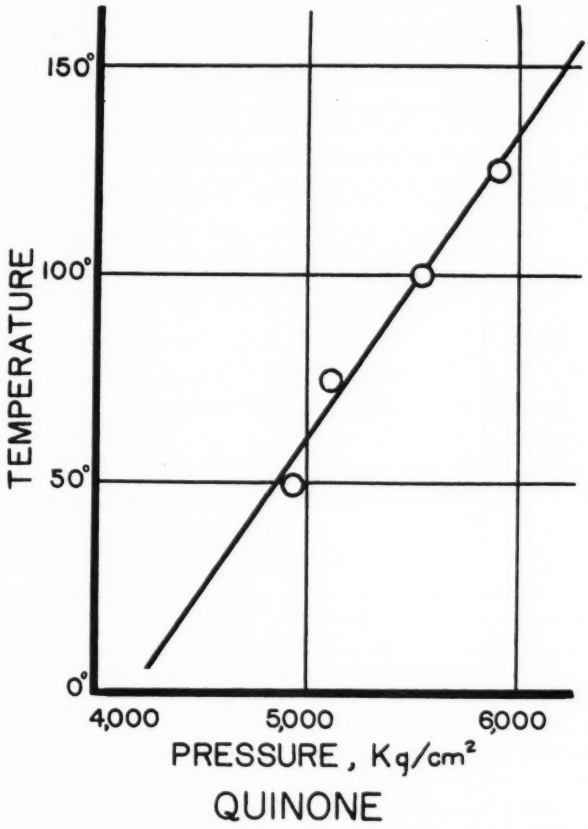

FIGURE 15. The transition pressures and temperatures of quinone.

values to consistency. I have not given in the table the parameters for the lines I–II, I–V, V–II, or V–III. These lines are sufficiently characterized by the parameters at their triple points. The lines II–III and III–IV appear to be curved, and detailed parameters are given for them in the table.

Quinone. Two set-ups were made: one with the smaller and one with the larger diameter cylinder. With the first set-up runs were made at room temperature, 150°, and 100°. A fairly large transition was found at the lower pressures, but nothing else to the maximum. No attempt was made to measure the parameters of the transition with accuracy, but this was reserved for the set-up with larger diameter. With this, runs were made at room temperature, 50°, 75°, 100° and 125°. At the two lower temperatures the transition runs sluggishly; at room temperature the sluggishness was so great that no attempt was made to get accurate values for either transition pressure

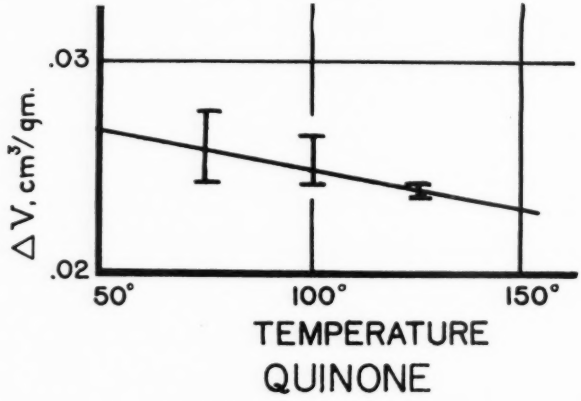

FIGURE 16. The volume changes of quinone as a function of temperature.

or change of volume. At 50° good values for the transition pressure were obtained, but the sluggishness made difficult measurements of the volume change, which accordingly were not attempted. At the remaining temperatures, good values were obtained for both parameters, with both increasing and decreasing pressure. The band of indifference is without appreciable width at these temperatures.

The pressure-temperature diagram is given in figure 15, the change of volume in figure 16, and the transition parameters in Table VIII.

The shearing curve rises with marked upward concavity for most of its extent, to a shearing strength of 5,500 kg/cm² at 50,000. Quinone under pressure has the highest shearing strength of any organic studied. The concavity begins indefinitely around perhaps 8,000, and

this may be connected with the transition, but the indication of a transition in this region is much more ambiguous than usual with shearing, and probably its existence would not have been suspected without the volume measurements. At the upper end of the shearing curve, above 40,000, there is a gentle downward break, which suggests another transition not found with the volume apparatus.

p-Dichloro-benzene. Four runs were made: the seasoning run at room temperature, and three runs on the 2,000 kg-2 minute schedule at 50°, 100°, and 150°. Irregularities were found on all three runs which probably mean a transition with very small volume change, not more than 0.0006 cm³/gm. The transition is asymmetrical, and was more obvious with increasing than with decreasing pressure. It runs in the neighborhood of 23,000 at 50°, 30,000 at 100°, and 38,000 at 150°. It is not by any means improbable that there is another small transition near this one.

TABLE VIII

TRANSITION PARAMETERS OF QUINONE

Pressure kg/cm²	Temperature Centigrade	$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
4,860	50°	.0724	.0270	120	2.82
5,550	100	.0724	.0250	129	3.02
6,240	150	.0724	.0230	135	3.15

Dichlorophenol. Three runs were made: the seasoning run at room temperature, a run at 50°, and one at 125°. There appears to be a small transition at comparatively low pressures, running asymmetrically, being much more marked with increasing than with decreasing pressure. With increasing pressure a transition with volume change 0.0010 cm³/gm ran at 14,000 at 50°, and at 15,000 at 125° with the same change of volume. On decreasing pressure the curvature is too great to permit good values, but irregularities were found at both 50° and 125° at a pressure somewhat higher than would be expected from the results with increasing pressure. In addition, there is fairly good evidence of another transition at 46,000 at 50° with ΔV equalling 0.0005; this is indicated by the readings with both increasing and decreasing pressure. At 125° there is also evidence of the same transition in approximately the same place, but the interpretation of the results is less satisfactory because of creep in the cylinder.

Hydroquinone. In addition to the seasoning run at room temperature, runs were made at 150° and 175°. There is a small transition,

running fairly symmetrically, without perceptible region of indifference. This runs at 17,000 at 150° and 21,500 at 175°, with volume change of approximately 0.0010 cm^3/gm. On the run at 150°, beginning at 28,000 or so, there was an irreversible decrease of volume extending over a pressure range of 6,000 kg/cm^2. This might be either leak or decomposition. There was, however, no apparent change in the appearance of the material at the conclusion of the run, and since the transition found at 150° was also found at 175° (it is true at higher pressure) and since the direction of volume change is the opposite of a normal decomposition, the probability seems to be that it was leak.

The shearing curve of hydroquinone has a gentle change of direction at pressures too low to measure in the apparatus, which possibly may be the transition found above carried down to room temperature. The shearing curve rises smoothly with gentle upward concavity for its entire measured length, reaching a strength of 5,000 kg/cm^2 at a pressure of 50,000. This is unusually high for an organic compound.

p-Toluidine. Two runs were made: the seasoning run at room temperature, and one at 150°. Nothing was found at room temperature, but at 150° two transitions were picked up, with changes of volume too small to determine accurately. Both transitions were picked up with both increasing and decreasing pressure, so that there appears to be little doubt about their existence. The transition I–II runs between 34,600 and 36,100, and II–III between 38,000 and 42,200. The change of volume of the two transitions was approximately the same, between 0.0010 and 0.0015 cm^3/gm.

Naphthalene. Runs were made with two different fillings of the apparatus; the first gave three runs from room temperature to 150°, and the second five runs between the same temperature limits. There is a small, but perfectly unmistakable transition in the general neighborhood of 30,000; no other transition could be found up to nearly 50,000. Readings were made on a time schedule of 2,000 kg/cm^2 increase of pressure in two minutes. The change of volume was so small that it was hopeless to try to land on the transition, and the regular time schedule was maintained through the transition. The transition phenomena are unsymmetrical, the transition running much more sharply with decreasing pressure than with increasing. In fact, at 75° and lower the transition was not perceptible with increasing pressure, but showed up definitely enough with decreasing pressure. At higher temperatures the point where the transition began with increasing pressure could be located as a break in the direction of the isotherm, rather than as a discontinuity in volume. This asymmetry persisted to 150°.

The experimental values for the equilibrium points are shown in Figure 17. The point at 75° lies off the line; since this point is more difficult to determine because of sluggishness of the transition, it was ignored in drawing the most probable transition line. The values for change of volume were scattering, varying irregularly between 0.0013 and 0.0027 cm^3/gm; 0.0020 is a fair enough average.

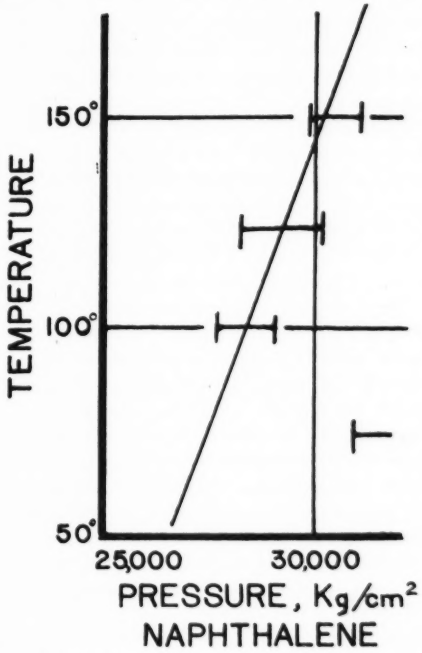

FIGURE 17. The transition pressures and temperatures of naphthalene.

The accuracy of the points does not justify making a formal table for the parameters. $d\pi/dp$ of the line shown in Figure 17 is 0.0285. With the value for ΔV just given this makes the latent heat of the transition vary from about 23 to 30 kg cm/gm.

The shearing curve has a gentle upward break between 25,000 and 30,000, which is probably the transition above. The general shape of the curve is gently concave upward, rising to a strength of 4,200 kg/cm^2 at 50,000.

d-Camphor. This was the natural product. I have already found camphor to have a very complicated phase diagram,[6] there being six modifications in the region between 0° and 200° and out to 12,000 kg/cm². In the present work, certainly three, and probably more new modifications were found, making nine or more in all, so that camphor has the richest polymorphic phenomena of any substance yet investigated, the next richest being water, with seven forms under pressure, and an unstable form at atmospheric pressure.

More than two full weeks were spent in the measurements on camphor, with two different set-ups. With the first set-up, eight different runs were made at temperatures from room temperature up to 200° and up to the maximum pressure, 50,000. These runs gave a fairly clean cut transition in the general neighborhood of 30,000, with other transitions in the range from 10,000 to 20,000 which were capricious and most puzzling to interpret. There was no evidence of other transitions out to 50,000. A second set-up was accordingly made in a cylinder with piston 3/8 inch in diameter instead of 1/4, permitting the use of greater quantities of material, and thus greater sensitiveness. With this, most careful measurements were made in the range out to 20,000, making seventeen different runs altogether in the range from solid CO_2 temperature up to 140°. Two of these runs were made by the method of slowly varying temperature at constant volume; the others were the conventional isothermals. Most of the measurements with the second set-up were made with extreme care in steps of 400 kg/cm², instead of the usual 2,000, so that the measurements were very time consuming. I think that the principal features of the pressu -mperature diagram are pretty well established by these measurements, although there are still some minor points, particularly in connection with the possible existence of unstable forms, which are not cleaned up. I was not willing to spend the much longer time that would have been necessary for this. Good values of ΔV were not obtained, however. The changes of volume are in general small, much smaller than in the previous work at lower pressures, the transitions are sluggish, capriciously super- or sub-press, and the transition obtained depends on the history, new forms often not appearing, but instead the point obtained may be between two modifications out of their domain of stability, on an unstable prolongation of a transition line. For this reason all that could be done was to get very rough values for ΔV, and no attempt at all was made to calculate the transition parameters. There is an additional complication, because when it is possible to combine transgressing the transi-

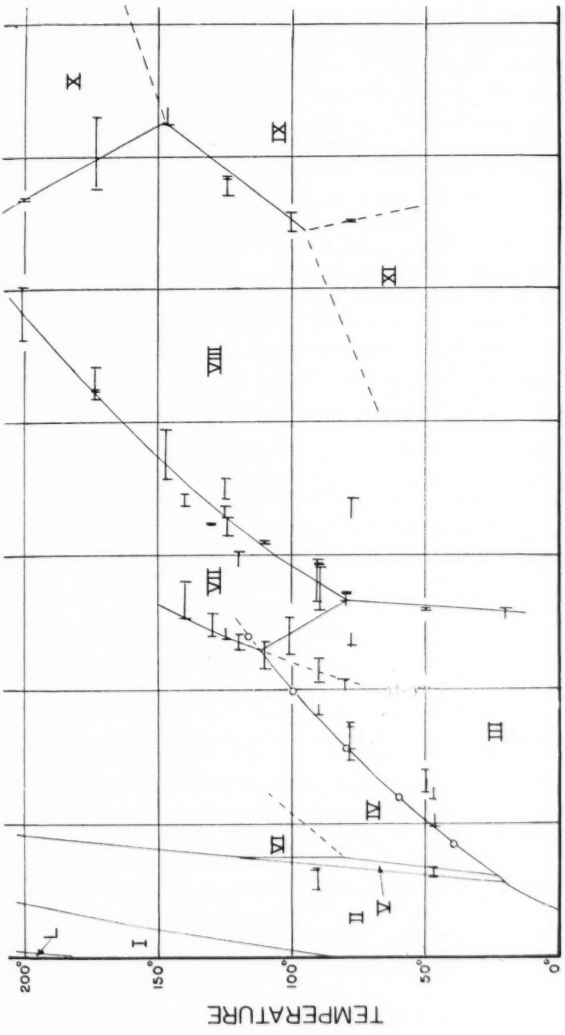

FIGURE 18. The transition pressures and temperatures of d-camphor. The modifications X and XI are not certainly established.

tion lines with a small interval of separation, there is the possibility of more than one transition running simultaneously in the apparatus. This doubtless occurred on several occasions.

The phase diagram (p–t) is shown in Figure 18. There are certainly three new modifications, VII, VIII, and IX, and with very high probability another, X. The existence of X is made probable by the abrupt change in direction of the line VIII–IX above 150°, the fact that the transition is more sluggish at 175° than at 125°, alone very strong evidence for the appearance of a new phase, and the smaller values of ΔV found at the two higher temperatures. The possible location of the hypothetical transition IX–X is shown dotted; if an experimental point could have been found on this line, of course the existence of the suspected modification would have been definitely established. It is also not at all improbable that the line VII–IX forks at the lower end, with a modification XI at lower temperatures; irregularities were found twice in the general region demanded by this.

Enough points were obtained on the line VII–VIII to make it highly probable that this line is not straight, but curved in the normal direction, as shown in the figure. VIII is distinctly more compressible than VII. The existence of the line IV–VII was not definitely established until measurements were made with the second set-up. At first I tried to force the transition points to lie on the known line III–IV. But the slope of the line was definitely wrong, and when points were obtained on the unstable prolongation of IV–VII into the region of III, the existence of the new phase VII and of the line IV–VII could no longer be doubted. After careful manipulation a couple of points were obtained on the line III–VII. III is not an easy phase to make appear, but IV or VII will usurp its place at the higher temperatures if either has been in the apparatus before. One has to approach the line from below and take pains not to get very far outside the region of existence of III if one wants to get it back again. The manipulations necessary to get this line involved holding the apparatus at pressures near 12,000 and at temperatures near 100° for a couple of days. Two points were obtained on III–VIII without great difficulty after the apparatus had been held at room temperature over night at low pressures to give III a chance to appear. At solid CO_2 temperature, pressure was increased from atmospheric to 12,000 without the transition to III running, but on warming, the internal viscosity became low enough to permit the transition to run with decrease of volume. A few points were also obtained on III–IV and on II–IV by way of orientation. The sensitiveness was not great enough to permit establishing the existence of V.

The following values of ΔV are very rough. In general, the order of magnitude of ΔV found with these two set-ups was only one half that found in the previous work to 12,000. On the line VIII–IX, ΔV is probably between 0.0025 and 0.0030 cm^3/gm. On the hypothetical VIII–X, ΔV drops to between 0.0015 and 0.0020. On IV–VII, ΔV is a very strong temperature function, decreasing from something of the order of 0.03 at 80° to perhaps 0.005 at 130°. At the triple point III–IV–VII, previous measurements gave for ΔV III–IV about 0.020. ΔV IV–VII must be larger than 0.020 at the triple point. No values of ΔV worth recording were obtained for III–VII. On the line VII–VIII, ΔV also appears to be a strong temperature function, varying with temperature in the inverse sense from that of IV–VII. From 80° to 200°, ΔV on VII–VIII increases perhaps from 0.005 to 0.015. Nothing worth recording was obtained for III–VIII.

One must be prepared for a more complicated state of affairs in camphor than in the simple phase diagrams of inorganic compounds. The great variation of ΔV along the transition lines is an example. As far as these measurements go, there is no definite evidence that the line IV–VII does not end in a critical point, an unprecedented state of affairs for a solid-solid transition. The sluggishness of the transitions is so great that there is no experimental evidence that the transitions may not be spread over a range, instead of taking place at a single well defined point. The possibility of various complexities suggested by recent discussions of transitions of the second, third, and higher orders must be kept in mind. Another possibility of complication presents itself in the fact that natural camphor is dextro-rotary; conversion to a left handed or a racemic form is to be kept in view. However, a measurement of the optical rotation, which I owe to the kindness of Professor Kohler, showed no difference within about 1 per cent limit of error between the rotation of the original specimen and the specimen used in the first set-up, which had been exposed to 50,000 and 200°.

The general course of the shearing curve of camphor is gently concave upward, but with three dips in the neighborhood of 7,000, 22,000 and 35,000 kg/cm^2. These dips doubtless correspond to the transitions above, but the correspondence is not close. The shearing strength at 50,000 is 4,200 kg/cm^2.

Menthol. In addition to the seasoning run at room temperature, runs were made at 75°, 100°, and 150°. There are probably at least three transitions, but the volume changes are not large, and they are sluggish at all temperatures, so that it would have been a matter of

very great difficulty to get data sharp enough to determine the transition parameters with any precision, and I let the matter go after

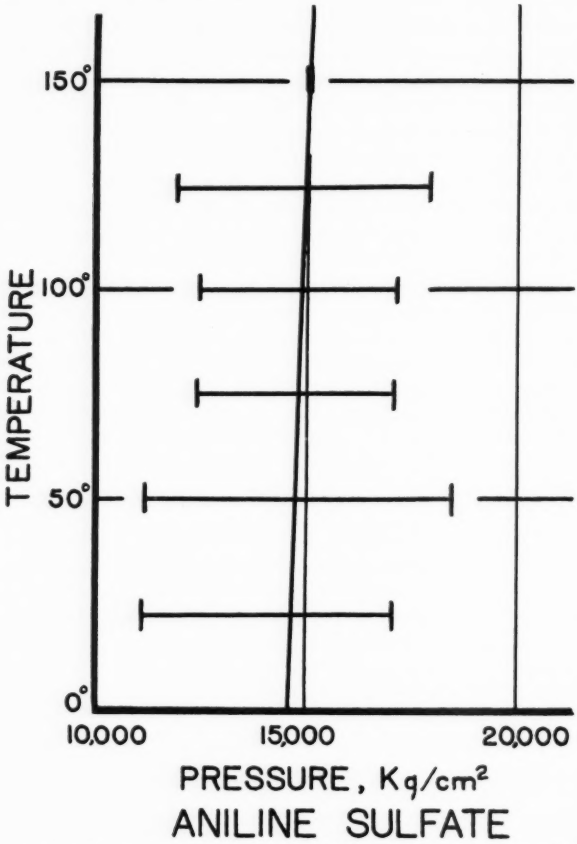

FIGURE 19. The transition pressures and temperatures of aniline sulfate.

more or less superficial examination. The transitions occur in the general neighborhood of 15,000, 30,000, and 42,000 kg/cm², and the transition lines run approximately vertically, with small latent heat. The two lower transitions are spread over a range of 7,000 to 10,000

kg/cm², and the upper transition over perhaps one half as much. The changes of volume are of the general order of 0.005 cm³/gm.

At atmospheric pressure it is known that menthol supercools very readily, and the crystallization phenomena are very sluggish. At one time I spent much effort in trying to produce large single crystals by crystallization from the sub-cooled melt, but with no luck whatever. The sluggish behavior under pressure is thus what might be expected.

Aniline Sulfate. Six runs were made with a single set-up, from room temperature to 150°. There is a single transition, running nearly vertically at approximately 15,000. The transition is highly unsym-

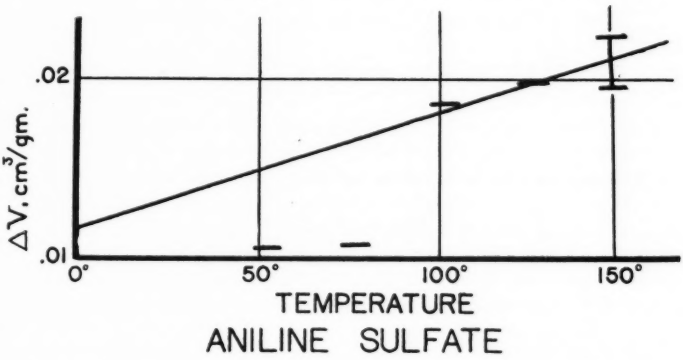

FIGURE 20. The volume changes of aniline sulfate as a function of temperature.

metrical, running much more sluggishly with increasing than with decreasing pressure. At the lower temperatures it was not possible to make settings on equilibrium, but measurements were made on a regular time schedule straight through the transition, and the beginning of the transition was detected by a slight break in direction of the isotherm. It was curious that the break in direction was not accompanied by a corresponding increase in creep. Because of the sluggishness, good values of ΔV could not be obtained at the lower temperatures. At higher temperatures the transition became sharper, permitting better values of ΔV with decreasing pressure. However, only at the highest temperature, 150°, was it possible to get values of ΔV with both increasing and decreasing pressure, and to set on equilibrium in the conventional way. Below 150° the band of in-

difference had a nearly constant width, and then at 150° the band narrowed to zero in an unusual way.

The pressure-temperature diagram is given in Figure 19, the changes of volume in Figure 20, and the transition parameters in Table IX.

TABLE IX

TRANSITION PARAMETERS OF ANILINE SULFATE

Pressure	Temperature	$\frac{d\tau}{dp}$	ΔV	Latent Heat	
kg/cm²	Centigrade		cm³/gm	kg cm/gm	gm cal/gm
14,500	0°	.3	.012	11	.3
14,750	75	.3	.016₅	19	.5
15,000	150	.3	.021	30	.7

There is obviously much uncertainty in ΔV and latent heat at low temperatures.

The shearing curve has a very definite upward break at 19,000, doubtless due to the transition above. Below and above the break the shearing curve is concave to the pressure axis. There is a second small upward break at 40,000. One suspects another modification at high pressures, suppressed in the volume apparatus by the same sluggishness that is so characteristic of the transition at 15,000. The shearing strength at 50,000 is 2,700 kg/cm². The general appearance of the shearing curve is linear, the curvature of the three different segments being only slight.

SUBSTANCES GIVING NEGATIVE RESULTS

The list of negative substances is surprisingly short in comparison with the number of negatives found among the inorganics.

Chloral Hydrate. Exploration to about 50,000 at room temperature and 45,000 at 150° in steps of 2,000 kg/cm² on the one minute schedule.

Trichloroacetamide. Exploration to 50,000 at room temperature and 47,000 at 125° in steps of 2,000 kg/cm² on the one minute schedule.

Guanidine Nitrate? Exploration at room temperature as in the last two examples. On trying for the exploration at 150°, the cylinder ruptured near the top and initial pressure, so that the evidence for or against a transition at this temperature is very meagre. The apparatus was not set up again.

Nitrourea. Three different set-ups were made with this. The first gave nothing at room temperature. Pressure was raised to 30,000 before raising temperature to 150°. From here pressure was raised to 45,000, and then released. A moderate sized transition appeared

to run at 30,000 on releasing pressure. At very low pressures there was some large volume increase. On again increasing pressure there was a large and abnormal decrease of volume in the low pressure range, then normal behavior up to 35,000, where the cylinder broke. The first repetition yielded nothing again at room temperature nor at 75° to 45,000, but on heating under 10,000 to 118° the contents exploded. A second repetition also yielded nothing on the seasoning run at room temperature. Pressure was now increased to 20,000 before raising temperature to 125°. Nothing new was found to 47,000. On releasing pressure volume creep (increase) started at 20,000. The direction of pressure change was at once reversed to an increase, and small steps made back to 40,000, but no reverse transition found, and there was a permanent increase of volume over the first excursion. The probability is then that there is no reversible transition, but the decomposition phenomena are complex. If the substance is heated at low pressures it explodes, but if heated at higher pressures there is non-explosive decomposition with increase of volume. There is an intermediate range of pressure in which the relation between the two types of decomposition is not simple.

Phenol. This is listed among the negative substances, although it is already known to have a transition in the general neighborhood of 2,000, because no further transitions were found with the present apparatus. Exploration was made to 50,000 at room temperature and to 45,000 at 150°, in steps of 2,000 on the one minute schedule.

Exploration with the shearing apparatus gave a pronounced knee at about 10,000, then nearly linear rise, but with slight upward concavity, to 3,300 at 50,000.

Anthracene. Exploration was made at room temperature and 150°. At room temperature the region between 20,000 and 34,000 was explored with particular care, taking readings every 400 kg, five times as many as usual. Nothing was found at either temperature.

The shearing curve takes a pronounced upward bend between 22,000 and 30,000, leading to the expectation of a transition. Below 25,000 the shearing curve is concave downward, above 25,000 concave upward, rising steeply to a shearing strength of 4,000 kg/cm^2 at 45,000. Between 45,000 and 50,000 the shearing curve turns and runs horizontally. This doubtless corresponds to the permanent change found at the termination of the shearing experiments, the anthracene being altered to a substance of deep purplish black color. This is the most strikingly obvious example found of an irreversible change of an organic substance by shearing. There was no obvious permanent

alteration in the material which had been exposed to hydrostatic pressure without shear.

Summary of Shearing Measurements on Substances not Investigated in Volume Apparatus

The arrangement in the following is alphabetical

Acetanilide. Shearing curve nearly linear over entire length, rising to 2,800 kg/cm^2 at 50,000.

Alizarin. Measurements were made only to 35,000, where the piston of the shearing apparatus broke. The shearing curve is gently concave toward the pressure axis up to 14,000 where there is an inflection, with gentle upward curvature beyond. The shearing strength at 35,000 is 1,800 kg/cm^2. A transition in the neighborhood of the point of inflection suggests itself.

Amidol. Shearing curve smooth, and with pronounced concavity toward the pressure axis over the entire length, rather unusual in an organic. The shearing strength at 25,000 is 2,600 kg/cm^2, and 3,900 at 50,000.

Aniline Hydrochloride. Beyond the "knee" at very low pressures the shearing curve is practically linear over its entire length, rising to 3,100 kg/cm^2 at 50,000.

Anthraquinone. The shearing curve is nearly linear up to 25,000; beyond this it rises with rapidly increasing upward curvature, reaching 3,300 kg/cm^2 at 50,000.

Dinitrotoluene. The shearing curve rises with gentle upward curvature to about 25,000, beyond which it rises linearly, reaching 2,900 kg/cm^2 at 50,000. Repetition gave essentially the same results.

Guanidine. The shearing curve is nearly linear beyond the knee at low pressures, and rises to 2,500 at 50,000. It is thus one of the weaker organic substances.

Picric Acid. The shearing curve rises with marked concavity toward the pressure axis, with increasing approach to linearity at the higher pressures, to 2,500 at 50,000.

Tartaric Acid. The shearing curve rises with gentle concavity toward the pressure axis to 5,000 kg/cm^2 at 50,000, the highest shearing strength found for any organic substance except quinone.

Summary

Transition data are presented for twenty-five organic substances in the pressure range up to nearly 50,000 kg/cm^2 and at temperatures between room temperature and 150° or 200°. It is obvious that our

theories of the structure of solids are not yet sufficiently advanced to justify an attempt to predict theoretically the values of the various transition parameters, so that for the present the material of this paper will have to be used qualitatively to suggest the general nature of the phenomena. As already suggested, polymorphism in the temperature range of this work is of much more frequent occurrence among organic than inorganic substances, but on the other hand the transition phenomena are less clean cut and definite, and are accordingly more difficult to measure. It is highly probable that a number of small transitions have been missed in the work above. The transitions of organic substances are in many cases highly unsymmetrical with respect to pressure above and below the equilibrium point. The statistical number of new transitions does not seem to be distributed as uniformly over the entire pressure range as it is with inorganics, there being too few at the higher pressures, and furthermore transitions with the larger volume changes seem to be disproportionately few at the high pressures. This is consistent with the very great increase in viscosity of organic substances to be expected at high pressure, as suggested both by measurements on the viscosity of organic liquids and on the shearing of organic solids. The effect is doubtless an interlocking effect, which will be more important with the more complicated molecules.

In addition to the transition measurements in the above, a study has been made of the shearing of a few organic substances as a function of pressure, and rough numerical data are given. The shearing curves of organics are much more frequently concave upward than those of inorganics; the explanation is doubtless the interlocking effect just mentioned.

I am indebted to my assistant Mr. L. H. Abbot for most of the readings, and for financial assistance to the Rumford Fund of the American Academy of Arts and Sciences, and to the Milton Fund of Harvard University. Comparatively prompt publication has been made possible by the Francis Barrett Daniels Fund of Harvard University.

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